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ONR DEPT. 33 SEA WARFARE AND WEAPONS

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Date: 7/20/2010

Fiscal Year 2010 Annual Report: 000140-81-10-5-2

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Contract Information

Contract/Grant Number: 000140-81-10-5-2
Contract/Grant Title: Solidification Based Grain Refinement in Steels
Program Officer: William Mullins

CO-PI Information

Number of Co-PIs: 0

Abstract

The overall research objective of this project is to determine suitable grain refiners for cast steels. Specific objectives are:

1) Identify possible phases to grow delta ferrite and austenite using current nucleation theory, crystallographic data, and thermodynamics.

2) Experimentally verify the effectiveness of possible nucleating compounds.

3) Extend grain refinement theory and solidification knowledge through experimental data.

4) Determine structure property relationships for the examined grain refiners.

5) Formulate processing techniques for using grain refiners in the steel casting industry.

During Fiscal Year 2010, this project worked on determining structure property-relationships. The testing primarily focused on adding or forming candidate phases from the previous project year into a plate casting. A series of experiments were also conducted to determine if the introduction of alloying elements that strongly segregate during solidification would reduce grain size. The plate castings were machined into tensile bars and metallographic samples. Tensile and hardness testing were done to quantify the effect of grain refinement on mechanical properties. Experiments with titanium found a reduction in ferrite and pearlite size which improved the yield and ultimate tensile strength. However, ductility was detrimentally impacted. Powder additions into the plate casting during pouring we not successful, except for NbO. NbO powder additions increased hardness in 1010 and 1030 through reduction in grain size. Misch metal and rare earth silicide additions have also reduced grain size and improved hardness.

Technical Section

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Progress Statement

In Fiscal Year 2010, the project worked on quantifying the structure-property relationship (Task 5) and developing industrially viable processing techniques (Task 6). Most of the effort has been centered on Task 5 due to experimental difficulties. The original experimental pattern consisted of four as-cast cylindrical tensile bar blanks. These castings exhibited significant amounts of microporosity that decreased elongation and strength. A plate casting with a large riser replaced the cylindrical castings for tensile bar blanks. The plate castings have dramatically lower levels of microporosity in them. Another difficulty found was that many of the powder additions did not cause refinement in these larger scale experiments. NbO additions were the only powder addition found to reduce grain size. Experiments were conducted to determine if titanium or rare earth additions could cause grain size reduction. Both have been successful for different reasons. Due to unforeseen difficulties in Task 5, work on Task 6 primarily centered around discovering methods which worked in the SVSU foundry. However, additions of NbO powder, FeTi, misch metal, and rare earth silicide were successful. Misch metal and rare earth silicide additions at the ladle are the most promising from an industrial stand point.

The project group has begun preparing for the remaining project tasks for the final year of the project. An

industrial trial of the rare earth silicide additions will be conducted (Task 7) with local foundries to determine if the grain refinement found in the laboratory occurs in the industrial setting. Most of the effort will be on examining grain refinement in stainless steels. A series of thermal analysis experiments in 304 and HK stainless steels with powder additions will assess the ability of the selected phases to reduce grain size (Task 8). In Task 9, phases that reduced the grain size in samples from the thermal analysis experiments will be used to refine the structure of plate castings. The plate castings will be sectioned into samples for metallographic and tensile testing. There are some samples remaining from the Fiscal Year 2010 experiments that are waiting for tensile testing, which will be done in the final project year.

Refereed Journal Articles

1. Tuttle, R.B., "Grain Refinement in Plain Carbon Steels," Transactions of the American Foundry Society, Vol. 118, pp. 425-436, 2010

2. Tuttle, R.B., "Examination of Steel Castings for Nucleation Phases," International Journal of Metalcasting

3. Tuttle, R.B., Role of Titanium on Grain Refinement of Steel Castings, International Journal of Metalcasting

4. Tuttle, R.B., "Grain Refinement in Plain Carbon Steels," Proceedings of the 114th Casting Congress, Orlando, Fl, April 2010

Books and Chapters

None entered

Technical Reports

None entered

Contributed Presentations

1. Grain Refinement in Plain Carbon Steels

Patents

None entered

Honors

None entered

Related Sponsored Work

1. Machinability of FeMnAl Alloys
   For: American Foundry Society (38,000.00)
   From: 9/1/2010 to: 6/30/2011

Major Ryan Howell who is part of the Army Research Laboratory developed a new class of iron-manganese-aluminum alloys as part of his doctoral work at Missouri University of Science and Technology. These alloys have an approximate chemistry of 30% Mn, 10% Al, 1% C, and 1% Si. The high manganese and aluminum content of these alloys ensures an austenitic structure at room temperature. Unlike traditional steels, these FeMnAl alloys develop strength through the precipitation of κ-carbide particles. The resulting mechanical properties can be strengths of 2,000 MPa, 80% elongation, and Charpy impact values of 221J. In 2009 these alloys passed ballistic testing for MIL-PRF-32269 perforated armor. In addition to these remarkable properties, the FeMnAl alloys are 12-18% lighter than low alloy steels and have significantly lower cost than current advanced high strength steels (AHSS). The high specific strength of these alloys makes these steels very attractive for a wide variety of military and transportation applications. Both automotive and aerospace applications would benefit from this alloy as an opportunity to reduce weight and increase fuel efficiency. However, these alloys are still not commercially available.

One impediment to employing these alloys is a lack of knowledge about their machinability. The effect of alloy composition on machinability has not been investigated. In fact, no data on machining these new alloys has been published. Nor is any current work on the appropriate cutting parameters or tool geometry being done. Since at some point any product made from these alloys would need some type of machining operation, resources would have to be devoted to elucidate the machining characteristics of these alloys. If this examination and investment had to be done as part of a product development cycle, it is unlikely that any company looking to use the FeMnAl alloys would be willing to adopt them.

By conducting a basic study of the machinability of FeMnAl alloys, companies will have valuable information that can be used in current and next generation military and transportation products. This project will also enable the development of cutting parameters and tooling geometry appropriate for these. As a direct result of this project and the partnership with Fullerton Tool, foundries will have a supplier of cutting tools that has previous experience with the FeMnAl alloys and suitable tooling. The ability to know that these alloys can be effectively machined would reduce the hesitancy in the marketplace to produce FeMnAl alloys. Therefore, the US military would be able to procure components made from multiple sources. Other possible users, such as the automotive and aerospace markets, would also have an understanding of the basic processing requirements and the necessary information to assist in selecting applications for these alloys.

2. Ultrasonic Testing Gauge R&R
   For: American Foundry Society (68,743)
   From: 5/1/2008 to: 5/31/2010
   As quality demands for steel castings continually increase, delivering the desired quality economically remains a challenge. Foundries have traditionally used radiography for quality testing. The reliance on this technique stems from its visual nature and historical precedent. For medium to large steel castings, radiography can become expensive. The expense results from the shielding, regulator requirements and acquisition cost of the highly radioactive source needed when penetrating six inches of steel. Ultrasonic testing (UT) can provide significant cost savings over radiography, because it has significantly fewer safety requirements and costs less than a high energy x-ray source. There is a strong need to determine the actual reliability of UT inspection and correlate it with current radiographic standards. Little data is available to scientifically evaluate this non-destructive evaluation technique. The goal of this project is to address both issues through a round robin style study.

ONR Statistics

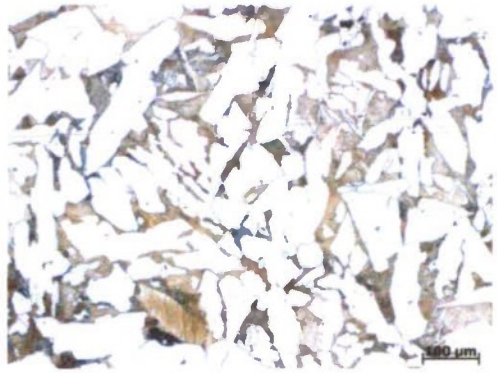
Papers Published: 2
Papers In Press: 2
Books/Chapters: 0
Books/Chapters In Press: 0
Technical Reports: 0
Invention Disciosures: 0
Patents Awarded: 0
Patents Pending: 0
Contributed Presentations: 1
Degrees Granted: 1
Honors: 0
Co-PIs: 0
Women Co-PIs: 0
Minority Co-PIs: 0
Graduate Students (Total): 0
Women Graduate Students: 0
Minority Graduate Students: 0
Undergraduate Students (Total): 2
Women Undergraduate Students: 0
Minority Undergraduate Students: 0
Post Doctoral Students (Total): 0
Women Post Doctoral Students: 0
Minority Post Doctoral Students: 0

Solidification Based Grain Refinement in Steels (Contract: 000140-81-10-5-2)

Objective:

1) Identify possible phases to grow delta ferrite and austenite using current nucleation theory, crystallographic data, and thermodynamics.
2) Experimentally verify the effectiveness of possible nucleating compounds.
3) Extend grain refinement theory and solidification knowledge through experimental data.
4) Determine structure property relationships for grain refiners.
5) Formulate processing techniques for using grain refiners in the steel casting industry.

1030 as-cast and no additions



1030 as-cast with NbO addition

Approach:

Using phases found to cause refinement in earlier experiments under this project, the current effort is to add or form these phases to act as heterogeneous nuclei within a test plate casting. These test plates are then sectioned for metallurgical examination , hardness and tensile testing. Experiments have been conducted in 1010, 1030, and 4130 in the as-cast state.

Scientific or Naval Impact/ Results:

This project will result in a better understanding of how nucleation occurs in various steels. The enhanced understanding of steel nucleation will provide the opportunity to manipulate it , which will enable the development of stronger cast steels through grain refinement . The long term goal for this line of research is to develop technology that could be adopted by industry for the U.S. Navy for lighter and stronger ships, aircraft, and vehicles.

20110930006

Abstract

The overall research objective of this project is to determine suitable grain refiners for cast steels. Specific objectives are:

1) Identify possible phases to grow delta ferrite and austenite using current nucleation theory, crystallographic data, and thermodynamics.
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During Fiscal Year 2010, this project worked on determining structure property-relationships. The testing primarily focused on adding or forming candidate phases from the previous project year into a plate casting. A series of experiments were also conducted to determine if the introduction of alloying elements that strongly segregate during solidification would reduce grain size. The plate castings were machined into tensile bars and metallographic samples. Tensile and hardness testing were done to quantify the effect of grain refinement on mechanical properties. Experiments with titanium found a reduction in ferrite and pearlite size which improved the yield and ultimate tensile strength. However, ductility was detrimentally impacted. Powder additions into the plate casting during pouring we not successful, except for NbO. NbO powder additions increased hardness in 1010 and 1030 through reduction in grain size. Misch metal and rare earth silicide additions have also reduced grain size and improved hardness.

Instructions: You may use this MS Word file to submit the Technical Section of the ONR End of Year Report. Please include any images, tables, graphs, and equations into the Technical Section of the report that you feel may strengthen the technical quality of your report. As in previous years, the Technical Section must include the *Technical Objectives*, *Technical Approach*, and *FY07 Progress (and Summary)*. Please complete the contract data section below so that technical information can be related to a specific contract.

Also, please save the file using the contract name as the file name (e.g. N00014-96-C-0387.doc). Instructions on sending the finished file are on the web site w3.sainc.com/onr33

If you have any questions with this form or with the web site, please contact the help desk at (703) 696-4022 or FY_07_EOY_Report@onr.navy.mil.

Contract Information

Contract Number	N00014-08-1-1052
Title of Research	Solidification Based Grain Refinement in Steels
Principal Investigator	Dr. Robert Tuttle
Organization	Saginaw Valley State University

Technical Section

Technical Objectives

The overall research objective of this project is to determine suitable grain refiners for cast steels. Specific objectives are:

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Technical Approach

The wrought steel industry has successfully developed high strength low alloy (HSLA) grades of steel. Strength is developed in HSLA steels by thermomechanical grain refinement and precipitation hardening. This is achieved by precipitating niobium carbides, which pin the austenite grains and prevent grain growth during thermomechanical processing.[1-20] Strengthening is achieved by a Hall-Petch strengthening mechanism and precipitation hardening.[1-20] The thermomechanical grain refinement originally developed for these grades has also been adopted for other steel grades.[20] Unfortunately, steel castings cannot undergo thermomechanical grain refinement because they are produced near net shape. In many cases, steel foundries refine the structure of a casting through heat treatment. The energy required for grain refining via thermomechanical processes or heat treatment impacts the environmental friendliness and cost effectiveness of these grades. A better approach is to create a small grain structure by manipulating the solidification of steels. This will result in a processing route that both steel mills and steel foundries can use to improve properties. Also, alloys other than the traditional HSLA alloys, such as stainless steels, could be strengthened this way.

Solidification based grain refinement has been successfully employed in aluminum, copper, magnesium, and cast iron alloys. When metals solidify, there must be stable nuclei for grains to grow. There are two possible nucleation routes: homogenous nucleation, which requires a large amount of undercooling, and heterogeneous nucleation, which requires a foreign nuclei.[21] Homogeneous nucleation occurs in a metal when the melt has cooled enough to allow atomically small embryos to form in the melt. Formation of these embryos requires a significant driving force, because a high energy interface is created when they form. Heterogeneous nucleation occurs when new grains grow on foreign nuclei. Foreign nuclei are either introduced as a solid phase in the melt or as a phase that precipitates in the melt. To be effective, the foreign particle must remain solid long enough to nucleate a new grain, have a similar crystal structure to the desired phase, and have a favorable interfacial energy between the foreign particle and desired phase.[21-23] Unlike other metals, the melting temperature of steel makes it difficult to find a phase that has the required lattice parameter and a sufficiently high melting point to remain solid during solidification. Additionally, the solid state reactions that form ferrite, pearlite, and for some alloys, austenite make it difficult to identify the structure present just after solidification.

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Progress Statement Summary

In Fiscal Year 2010, the project worked on quantifying the structure-property relationship (Task 5) and developing industrially viable processing techniques (Task 6). Most of the effort has been centered on Task 5 due to experimental difficulties. The original experimental pattern consisted of four as-cast cylindrical tensile bar blanks. These castings exhibited significant amounts of microporosity that decreased elongation and strength. A plate casting with a large riser replaced the cylindrical castings for tensile bar blanks. The plate castings have dramatically lower levels of microporosity in them. Another difficulty found was that many of the powder additions did not cause refinement in these larger scale experiments. NbO additions were the only powder addition found to reduce grain size. Experiments were conducted to determine if titanium or rare earth additions could cause grain size reduction. Both have been successful for different reasons. Due to unforeseen difficultics in Task 5, work on Task 6 primarily centered around discovering methods which worked in the SVSU foundry. However, additions of NbO powder, FeTi, misch metal, and rare earth silicide were successful. Misch metal and rare earth silicide additions at the ladle are the most promising from an industrial stand point.

The project group has begun preparing for the remaining project tasks for the final year of the project. An industrial trial of the rare earth silicide additions will be conducted (Task 7) with local foundries to determine if the grain refinement found in the laboratory occurs in the industrial setting. Most of the effort will be on examining grain refinement in stainless steels. A series of thermal analysis experiments in 304 and HK stainless steels with powder additions will assess the ability of the selected phases to reduce grain size (Task 8). In Task 9, phases that reduced the grain size in samples from the thermal analysis experiments will be used to refine the structure of plate castings. The plate castings will be sectioned into samples for metallographic and tensile testing. There are some samples remaining from the Fiscal Year 2010 experiments that are waiting for tensile testing, which will be done in the final project year.

Progress

Powder Addition Effects

The first series of experiments conducted were simple powder additions of heterogeneous nucleating phases identified in the first year of the project. Sixty pounds of 1010, 1030, or 4130 were melted in a 3kHz induction furnace. The melt was brought to 3,100°F. Alloying elements were added to the melt prior to tapping. The furnace was tapped into the ladle where a final aluminum deoxidation addition was made. A final temperature check was done to ensure the liquid steel was at the target pouring temperature of 2950°F. Five grams of each powder addition were placed in the runner of the green sand mold prior to mold closing. All of the powders used were -325 mesh in size. The steel was poured into the mold and then allowed to cool for one hour before shakeout. Once cooled to room temperature, the gating system was removed and the cylindrical bars were machined into ½ inch diameter tensile bars. Tensile testing and metallographic examination were conducted on the bars. Initially, no significant increase was found

for the first powders examined (See Figures 1 and 2). It was thought that the powder placed in the runner was not able to enter the cylindrical test sections in the mold. Powder additions were placed inside the cylindrical bars, which also resulted in no increase in properties or change in microstructure. Another series of experiments were done to examine if adding the powder in the downsprue during pouring provided sufficient mixing of the experimental powder and the steel. Again, there was no change in properties or microstructure observed. A final series of experiments were poured with larger powder additions, which also resulted in no increase in strength.

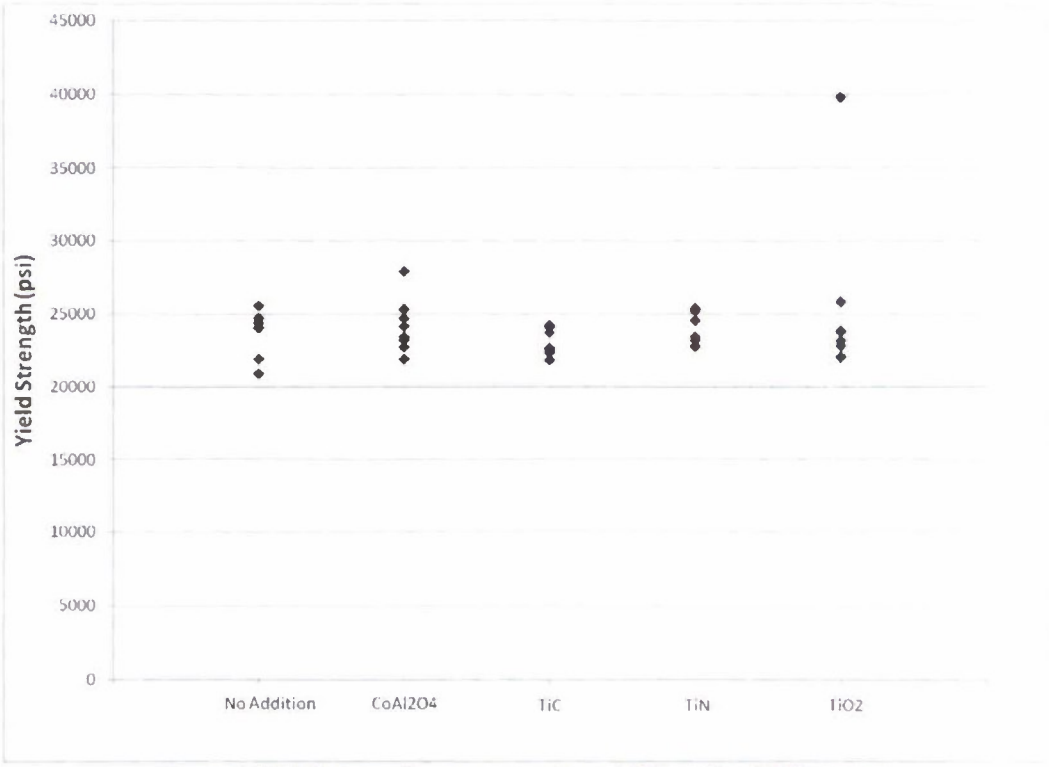

Figure 1 Yield strength verses powder additions for 1010 as-cast.

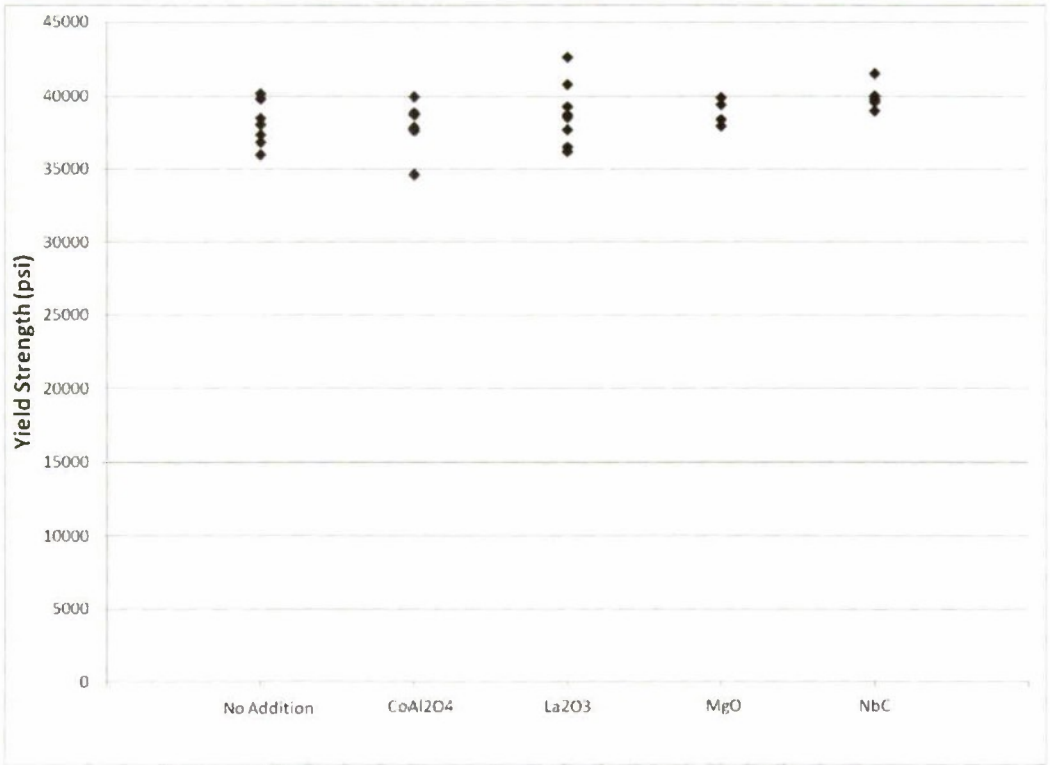

Figure 2 Yield strength verses powder addition for 1030 as-cast.

The PI has not come to a definitive conclusion why these initial powder additions produced refinement in the earlier thermal analysis (TA) experiments, but not in the test castings. There are two possible explanations. First, that the powder additions in the TA experiments were so large relative to the mass of steel being poured that there were a larger number of favorably oriented nuclei that could assist solid steel growth. In the test casting experiments, the powder addition was relatively smaller, which created fewer favorable nuclei. The second possibility is that because the cooling rate is slower in the test casting, there was insufficient undercooling to drive nucleation on the nuclei provided by these powders.

NbO was not experimented with in the initial TA experiments. However, the PI realized that its formation might explain some of the results from the NbC additions in the TA experiments. Thermodynamically NbC should not remain solid in liquid steel. It was hypothesized that instead of NbC acting as a favorable nuclei that some of the NbC could have oxidized to form NbO while filling the TA cups. NbO also has a favorable crystallographic match with δ-ferrite.

For the NbO addition experiments, fifty pounds of 1010 or 1030 were melted in a 3kHz induction furnace and brought to 3,100°F. Alloying elements were added to the melt before tapping into a ladle where a final aluminum deoxidation addition was made. A final temperature check was done to ensure the molten steel was at the 2950°F pouring temperature. The test casting was a 1inch by 5 inch by 10 inch plate. Five grams of NbO powder was added in the first mold and 10g was added to the second mold. The powder addition was done by adding the -325 mesh powder in the downsprue during pouring. The steel cooled for one hour before shakeout. Once cooled to room temperature, the gating system was removed and the casting sectioned into 1 inch square, 5 inch long tensile bar blanks. These blanks were then machined into ½ diameter tensile bars for testing. One bar from each plate was sectioned for hardness testing and metallographic examination.

Table 1 summarizes the Rockwell B hardness measurements for 1010 and 1030. There was a significant increase in hardness with NbO additions. Both steels were harder when more NbO was added.

Table 1 Rockwell hardness measurements for NbO powder additions.

Alloy	Hardness (HRB)
1010	42.58
1010 5g NbO	67.82
1010 10g NbO	71.56
1030	74.08
1030 5g NbO	78.66
1030 10g NbO	82.96

A dramatic decrease in grain size was observed in the samples with an NbO addition (See Figures 3-8). This corresponds with the hardness increases observed in Table 1. 1010 responded with a significantly larger grain size decrease and hardness increase. The small amount of pearlite in the 1010 structure is likely the reason for it being more responsive to grain refinement. Pearlite is a strong phase. Its amount is primarily controlled by the amount of carbon in the alloy. 1030 forms more pearlite which would explain why the observed increase in hardness is not as large. One interesting observation made in the 1030 samples was a change in ferrite grain shape. Comparing Figures 6 and 7 does not reveal a significant change in size. However, the ferrite in the NbO containing samples is more rounded and equiaxed than the plain 1030 sample. Examination of Figure 8 shows that the larger NbO addition resulted in a finer grain size.

At this time, the PI is awaiting tensile testing results to determine the effect these changes have on properties.

Figure 3 Micrograph of as-cast 1010 without any additions.

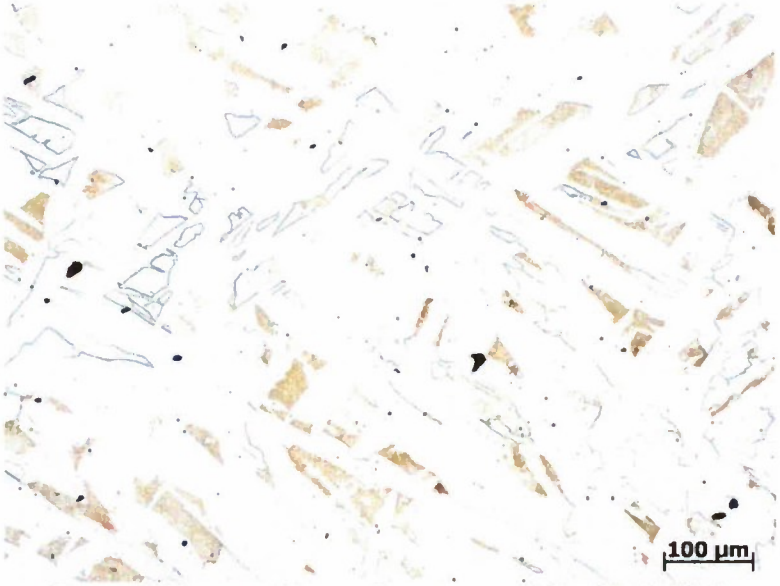

Figure 4 Micrograph image from as-cast 1010 with 5g NbO.

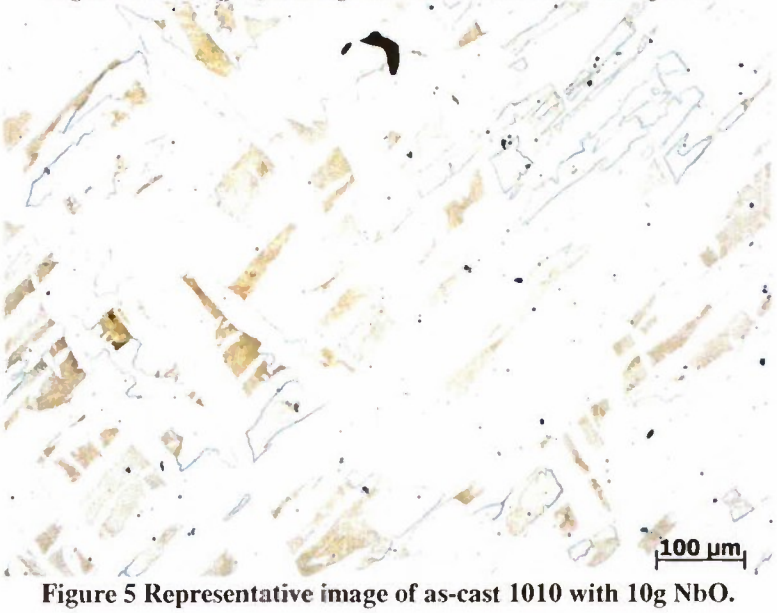

Figure 5 Representative image of as-cast 1010 with 10g NbO.

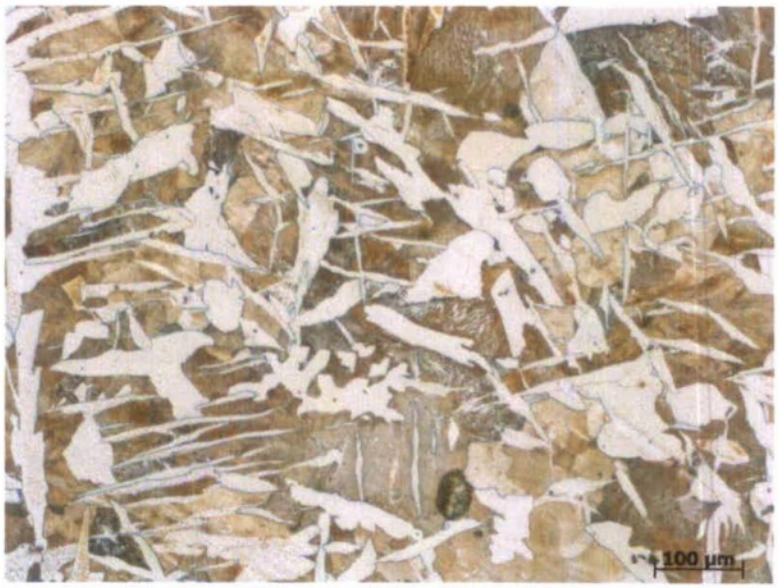

Figure 6 As-cast 1030 with noaddition.

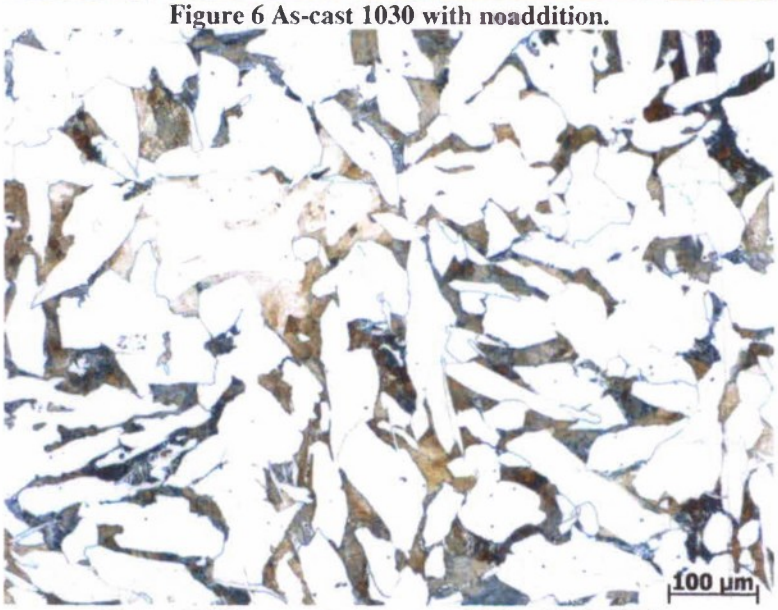

Figure 7 Micrograph of as-cast 1030 with 5g NbO.

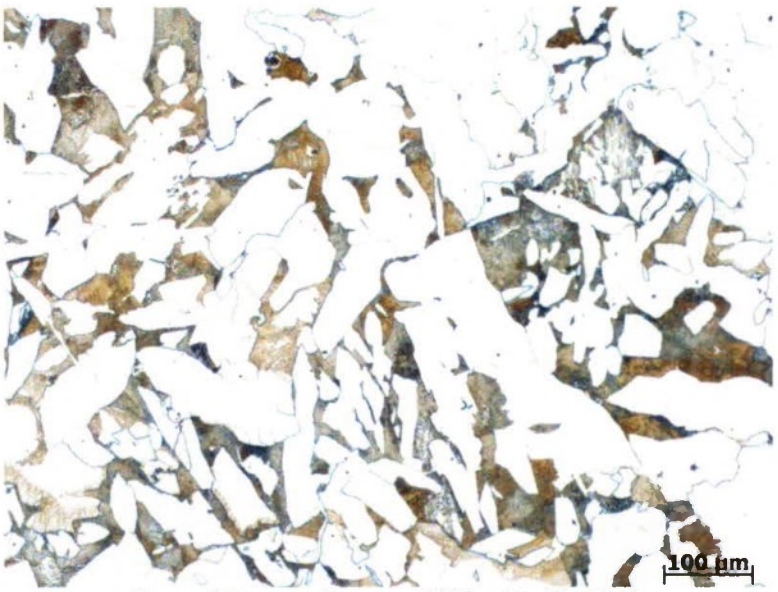

Figure 8 Image of as-cast 1030 with 10g NbO.

Titanium Additions

Grain refinement is based on the idea of introducing heterogeneous nuclei into the melt. These nuclei provide sites within the melt for solid steel to bond to, thereby reducing the energy required for creating a solid metal in the liquid. Heterogeneous nuclei must satisfy the following three conditions: be solid at the melting point of the host metal, the melt must wet the surface of the particle, and there must be matching crystallographic planes between the nuclei and host metal for bonding.[1-4] Typically, candidate phases are selected by examining the first and last criteria listed since wetting data is frequently unavailable. Crystallographic matching is usually done by examining the lattice parameter mismatch between the candidate phase and the solid crystal structure of the host metal on different cyrstallographic planes (See Equation 1).[5]

$$\delta^{(hkl)_s}_{(hkl)_n} = \sum_{i=1}^{3} \frac{\left|\left(d^{i}_{[uvw]_s} \cos\theta\right) - d^{i}_{[uvw]_n}\right|}{d^{i}_{[uvw]_n}} * 100 \qquad \text{Equation 1}$$

Where $(hkl)_s$ is a low-index plane of the substrate, $[uvw]_s$ is a low-index direction in $(hkl)_s$, $(hkl)_n$ is a low-index plane in the nucleated solid, $[uvw]_n$ is a low-index direction in $(hkl)_n$, $d_{[uvw]n}$ is the interatomic spacing along $[uvw]_n$, $d_{[uvw]s}$ is the interatomic spacing along $[uvw]_s$, and
θ is the angle between the $[uvw]_s$ and $[uvw]_n$. Candidate phases that have a lattice disregistry less than 12% have been found to act as effective nuclei.[1-5]

Work in aluminum alloys has found strongly segregating elements can play an important role in assisting heterogeneous nucleation and grain refinement.[6-9] Experimental data has found that grain refinement dramatically increases when certain alloying elements exceed a critical value. Observations of cast verses wrought aluminum alloys have found that the cast alloys often respond better to grain refinement additions.[2,7] The current theory is that the solute elements involved strongly segregate to the liquid during solidification. The resulting difference in liquid composition changes the liquidus temperature of the alloy and reduces grain growth. The change in liquidus temperature is thought to increase the amount of

constitutional undercooling which provides a larger driving force for heterogeneous nucleation.[10] Growth restriction by a particular alloying element can be determined using Equation 2.[10]

$$GRF = mc_o(k-1) \qquad \text{Equation 2}$$

Where m is the gradient of the liquidus, c_o is the concentration of the solute in the alloy, and k is the partition coefficient. Partition coefficients are determined by the following equation:

$$k = \frac{c_s}{c_l} \qquad \text{Equation 3}$$

where c_s is the composition of the solid and c_l is the composition of the liquid at the temperature of the solidification front.[10]

Experimental Procedure

A high frequency induction furnace was used to melt 50 lbs of 1030 steel. 1020 steel scrap was used to form the charge. Carbon and ferromanganese were added to the heat once it reached 3000°F. The melt was tapped at 3120°F into a preheated ladle where aluminum was added for deoxidation. For the heats with titanium, ferrotitanium was added with the aluminum in the ladle. The green sand molds were then poured at a temperature of approximately 2950°F. The chemistry for each heat is listed in Table 2. The target titanium levels were 0%, 0.1%, and 0.3%.

Table 2 Chemistry for steel heats poured.

Heat	C (wt. %)	Mn (wt.%)	Si (wt.%)	Cr (wt. %)	Mo (wt. %)	Al (wt. %)	Ti (wt. %)
No Ti	0.41	0.76	0.094	0.052	0.014	0.085	0.0012
0.1 Ti	0.41	0.58	0.058	0.097	0.018	0.097	0.075
0.3 Ti	0.36	0.60	0.10	0.10	0.020	0.10	0.20

In addition to varying the titanium level, castings were poured from each heat with powders thought to act as heterogeneous nuclei. Five grams of -325 mesh powder was placed in the runner of the test casting (See Figure 9). La_2O_3, MgO, and NbC were selected as candidate materials based on previous work by the author.[19] These materials have a low lattice disregistry with austenite and reduced undercooling in previous thermal analysis experiments.[19] TiC and TiN were not used since the goal was to determine how titanium affected heterogeneous nucleation. Including TiC and TiN would have made it difficult to determine how the segregation of titanium affected grain refinement.

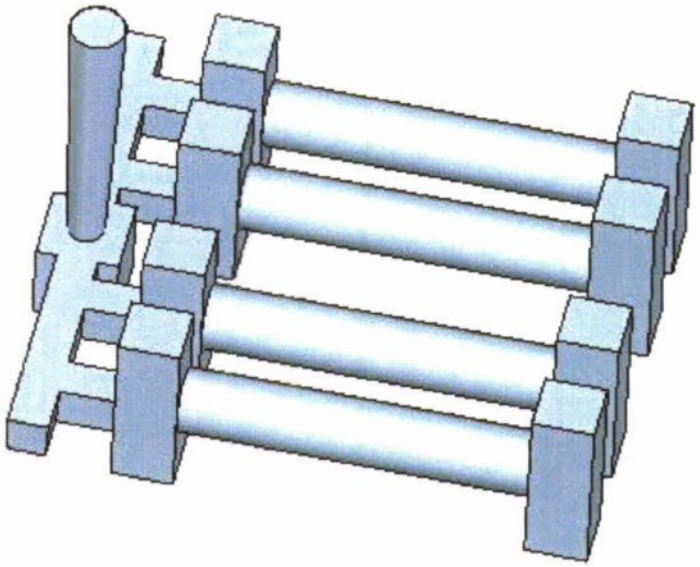

Figure 9 Round tensile bar patter employed in these experiments.

Once the castings were poured, they were allowed to cool for a hour and a half before shakeout. The casting temperature at shakeout was around 1,000°F. Then, the castings cooled to room temperature before further processing. The rigging system was removed, and the resulting cylinders were machined into 0.5 inch diameter test bars according to ASTM E8. No heat treatment was done to the bars. Tensile testing was conducted on a hydraulic tensile testing machine with an extensometer in accordance with the previously mentioned standard.

Metallographic samples were sectioned from the fractured tensile bars. They were mounted and polished using a semi-automatic polisher. Grinding was done with 180, 320, and 600 grit SiC paper with water. Polishing was completed with 6 μm and 1 μm diamond suspensions with a final polish of 0.05 μm alumina. A 2% nital solution was used to etch the samples.

Results and Discussion

Figures 10-12 illustrate yield strength (YS), ultimate tensile strength (UTS), and percent elongation of the tensile bars. There are two striking trends in the data. First, the addition of the powders did not significantly affect the strength at any titanium level. The addition of titanium did not appear to assist heterogeneous nucleation, because the bars that contained titanium and a nucleating phase did not have a higher strength than the bars with no addition. The second striking trend is that the YS and UTS increased with titanium content. There is significant scatter in the percent elongation data. Figure 4 reveals a significant drop in ductility with 0.3% titanium. It is difficult to determine if there is a difference between the no titanium samples and the 0.1% titanium samples. The ductility for all the samples is low compared to production steels.

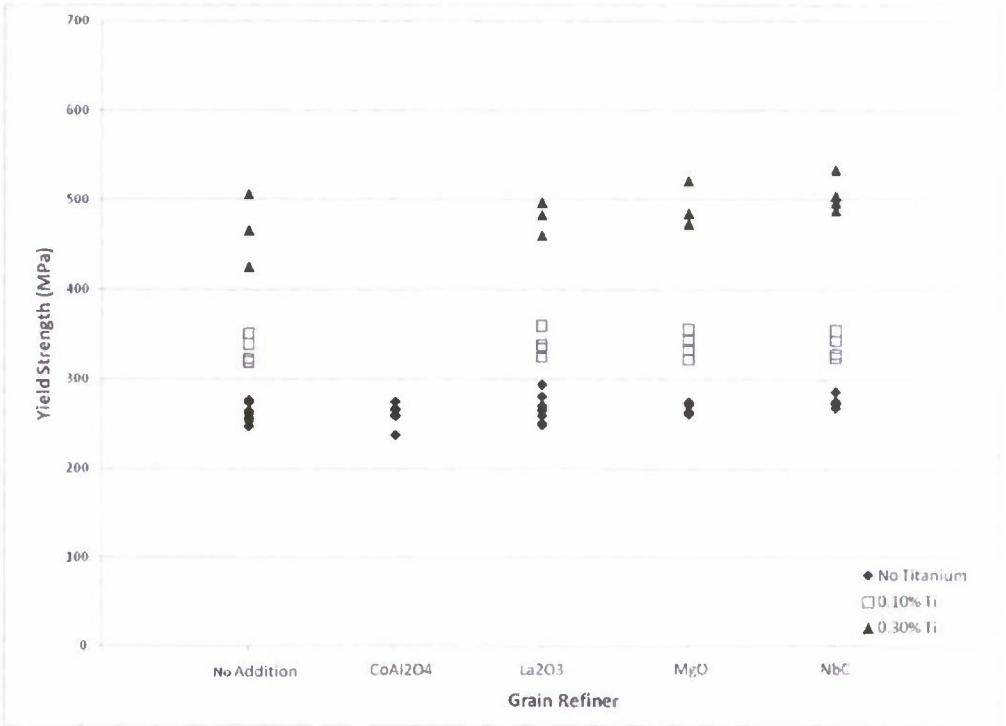

Figure 10 Yield strength as a function of titanium level and powder addition.

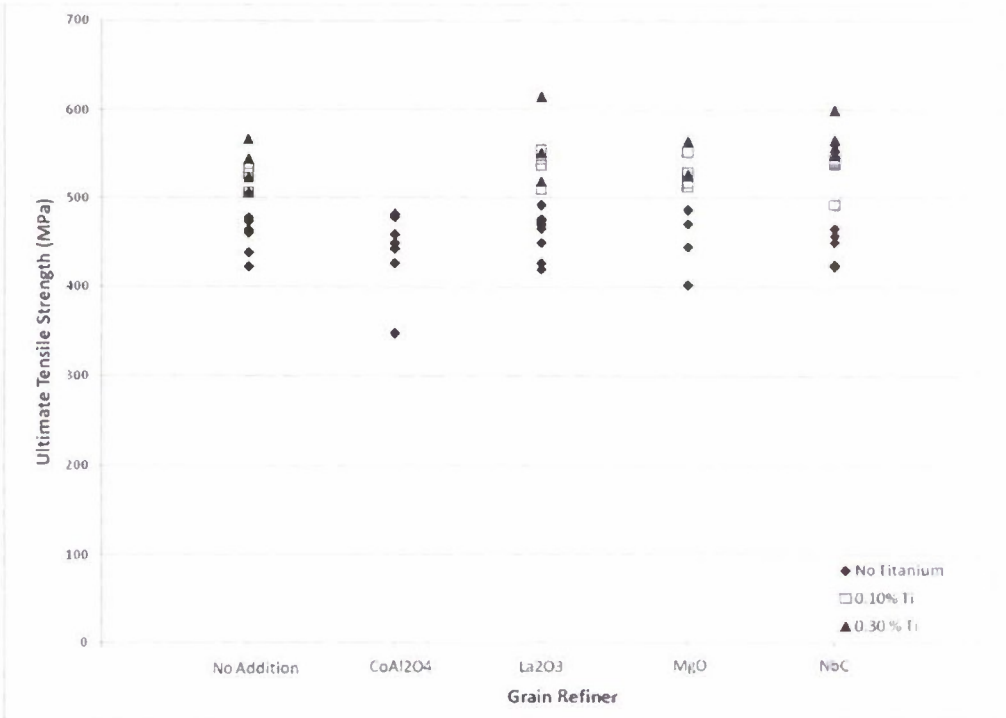

Figure 11 UTS of the tensile bars as a function of titanium and powder additions.

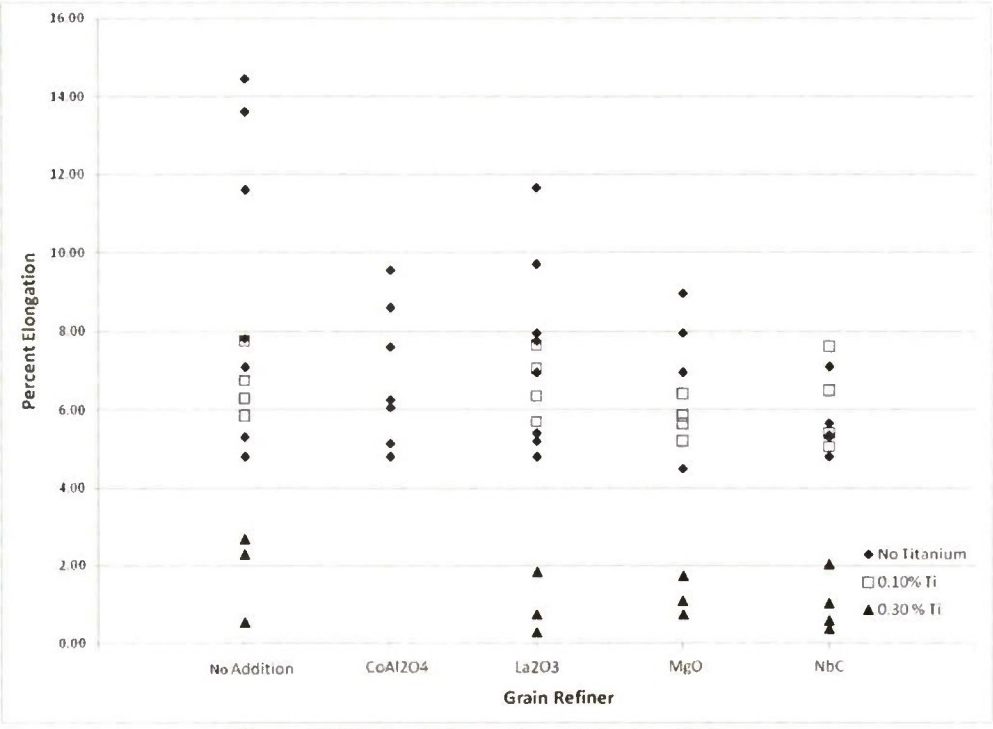

Figure 12 Percent elongation of the tensile bars.

Microscopy Results

There was a dramatic change in ferrite shape in the titanium containing samples. In the no titanium sample, the observed ferrite shape tended to be acicular (See Figure 13). The ferrite had a more rounded shape in the titanium containing samples (See Figure 14 and 15). While it is hard to determine if the size is smaller, the more compacted shape of the ferrite probably created a shorter distance for dislocations to move through before being blocked by a grain boundary thus strengthening the steel.

Significant amounts of microporosity were observed in the tensile bars. Figure 13 has several large pores visible. Image analysis on unetched micrographs determined the average size of the microporosity was 39 $\mu m \pm 27\ \mu m$. The large amount and size of microporosity in these tensile bars would account for the low ductility observed in these samples.

Figure 13 Etched micrograph of the no titanium, no addition tensile bar.

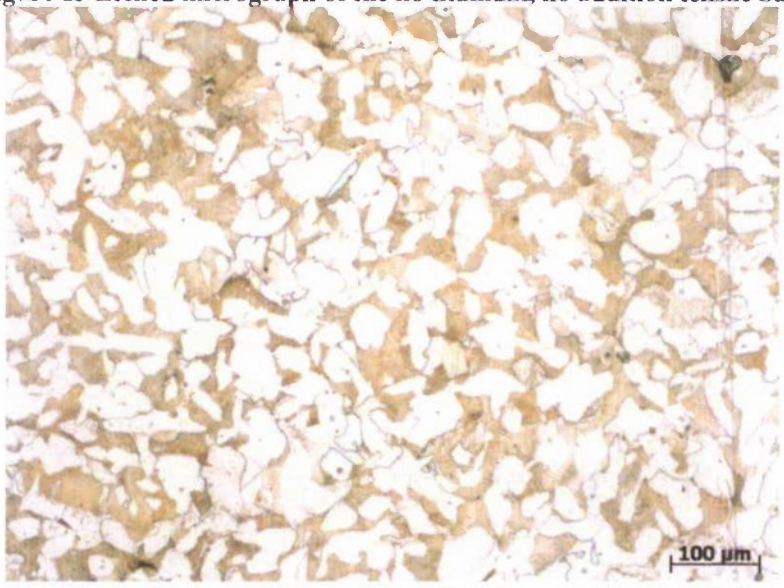

Figure 14 Etched micrograph of the 0.1% Ti, no addition tensile bar.

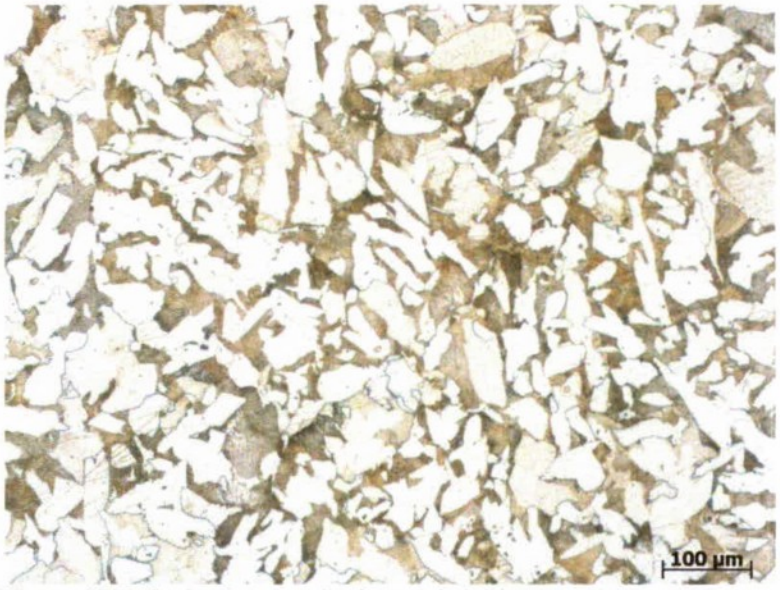

Figure 15 Etched micrograph of the 0.3% Ti, no addition tensile bar.

To determine the cause of the microporosity, the tensile bar casting was simulated in a casting simulation package. The prediction of microporosity can be done using the Niyama criteria (See Equation 4). Values below 0.70 have been found to cause microporosity in steels.[4]

$$N_y = \frac{G_T}{\sqrt{\frac{dT}{dt}}}$$

Equation 4

Where N_y is the Niyama criteria, G_T is the thermal gradient in the casting, and dT/dt is the cooling rate of the region of the casting being examined.

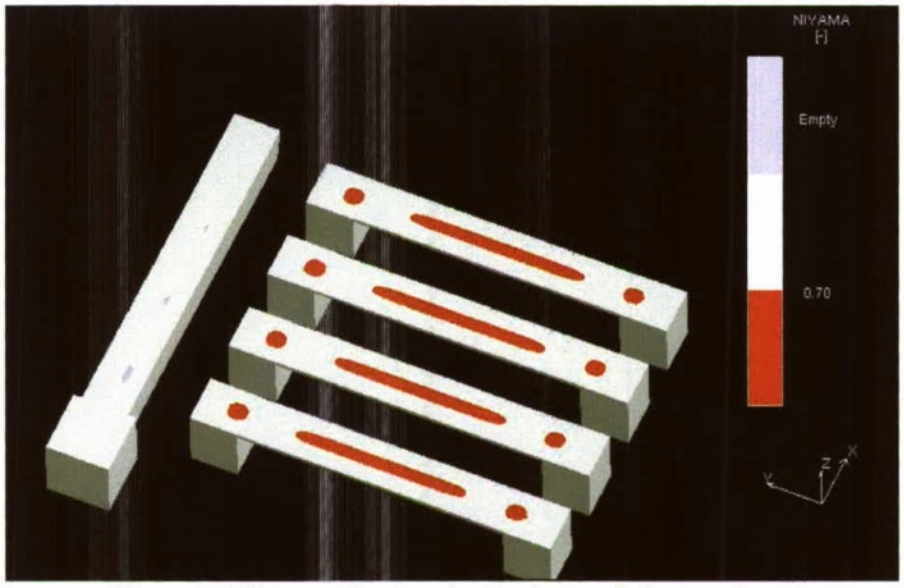

Figure 16 Niyama criterion plot for the tensile bar castings.

Figure 16 depicts the regions above and below the critical Niyama criterion value of 0.70. The red regions correspond to areas likely to form microporosity. It is evident from these simulation results that the

casting was prone to microporosity formation within the center of the tensile bar gauge section. This correlates with the location of the metallographic samples. The microporosity resulted in the observed reduction in elongation.

Plate Casting Results

Due to the low elongation in all the samples, a second set of samples were made by pouring a 1 inch thick, 5 inch wide, 10 inch long plate. The plate had a riser to eliminate shrinkage porosity. Since the elongation of the 0.3% Ti bars was obviously lower than the no titanium bars, only a no titanium and 0.1% titanium plate was made. Based on the results from the tensile bars, neither plate contained any powder additives. Tensile bars were then machined from the plate according to ASTM E8.

The 0.1% Ti plate had a higher YS and UTS than the no titanium plate (See Figures 17 and 18). Unlike the relationship shown in Figure 12, the elongation of the majority of the 0.1% titanium bars was lower than the no titanium bars (See Figure 19).

Figure 17 Yields strength for the tensile bars made from cast plates.

Figure 18 UTS for the cast plate tensile bars.

Figure 19 Percent elongation for the tensile bars from the plate castings.

Microscopy of the tensile bars found a similar structure change to that observed in the initial tensile bars. The ferrite shape in the no titanium plate was more acicular than the 0.1% titanium containing bars (See Figures 20 and 21). Image analysis determined an average microporosity size of 13 μm ± 6 μm. This is significantly smaller microporosity than the initial tensile bars and accounts for the higher elongation. The smaller variation in micropore size likely contributed to the smaller variation in elongation among the tensile bars.

One of the 0.1% tensile bars had a higher elongation than the other bars (See Figure 19). Figure 22 is a representative micrograph for that sample. The ferrite appears to be smaller than the ferrite in the other 0.1% titanium bars. This was unexpected since the tensile bars come from the same plate. It is possible that the 0.1% titanium bar in Figure 22 came from the front edge of the plate. This area is farthest away from the riser and cools faster than the regions closer to it. However, no significant difference was observed in the microstructure of the no titanium containing tensile bars. It was also not possible to confirm that the bar in Figure 22 came from that region since the location of each bar within a plate was not recorded.

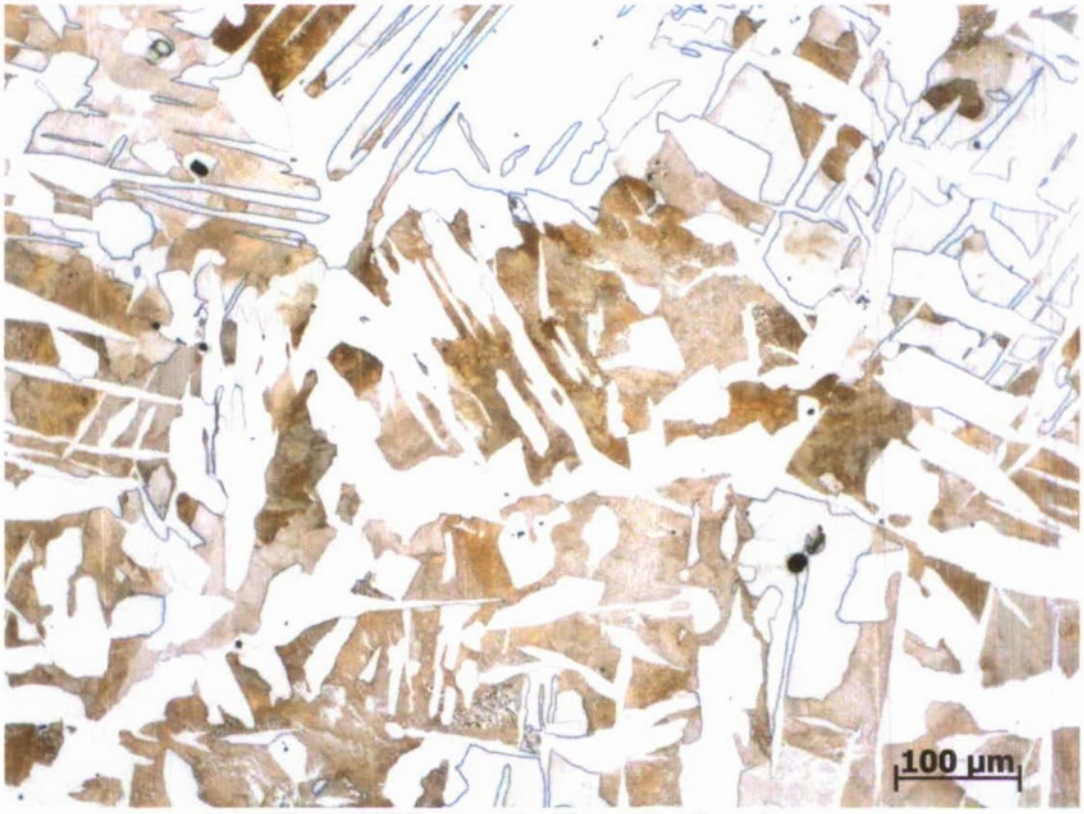

Figure 20 Micrograph of the no titanium plate.

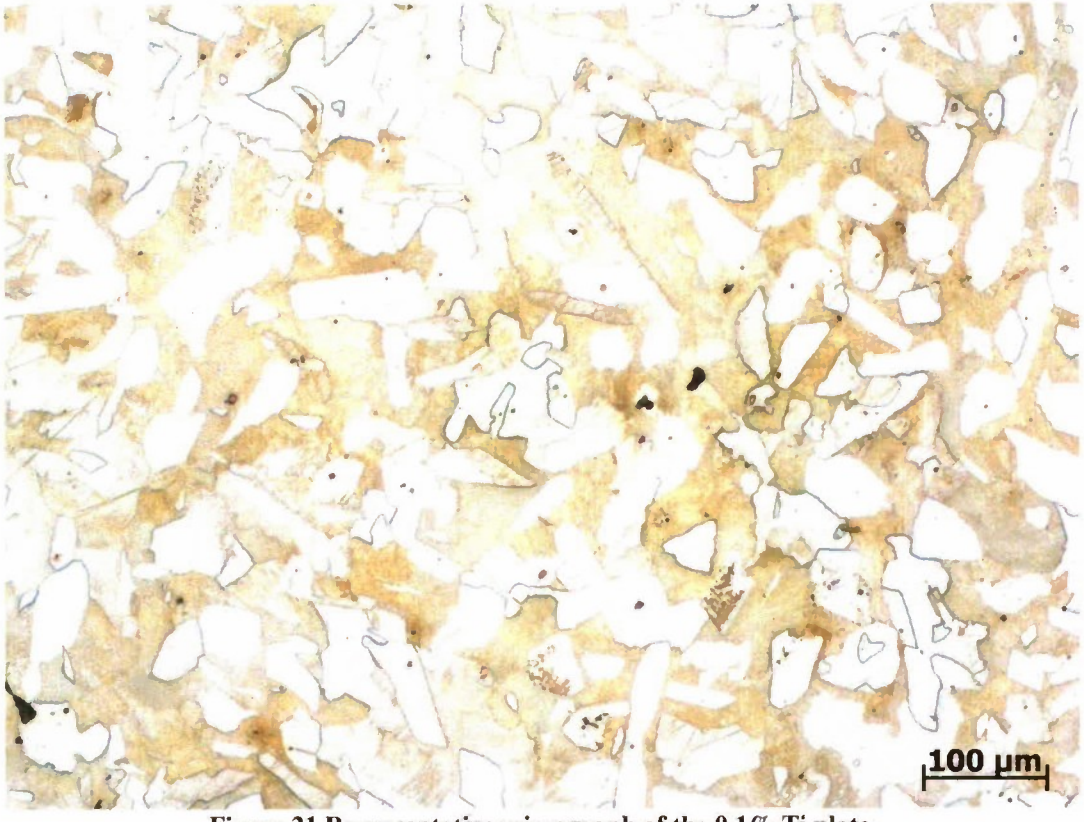

Figure 21 Representative micrograph of the 0.1% Ti plate.

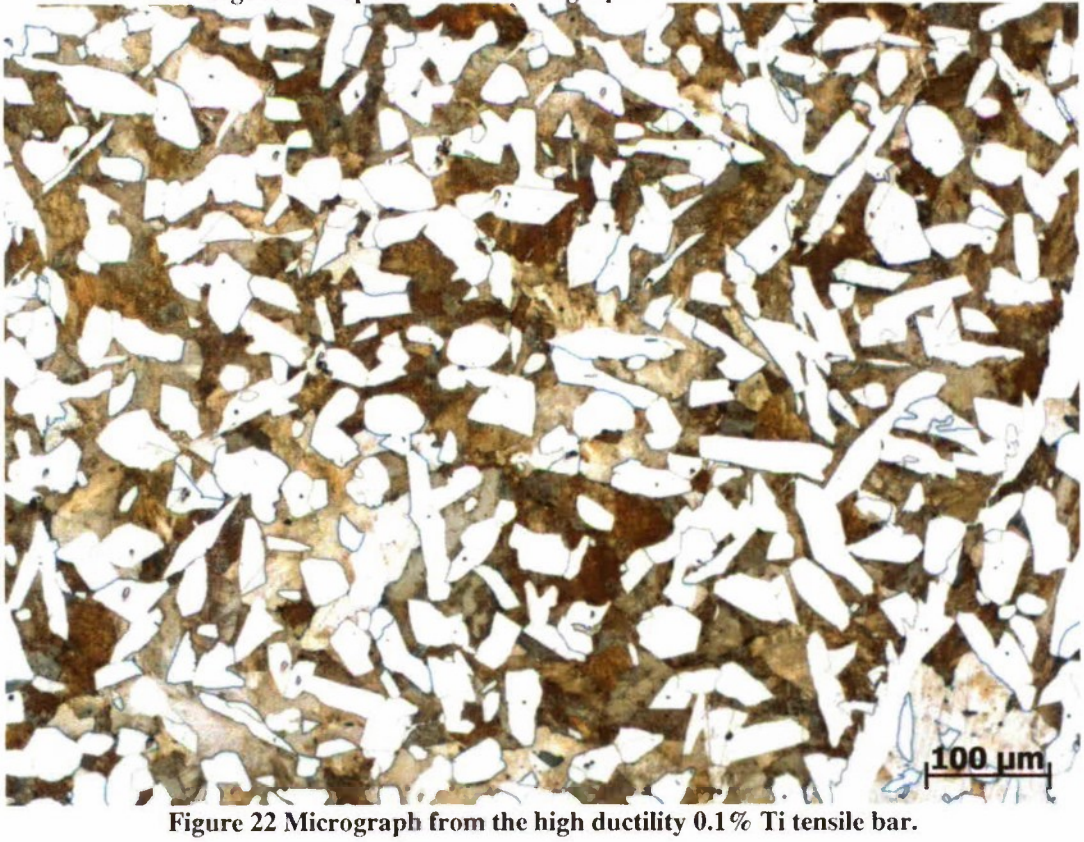

Figure 22 Micrograph from the high ductility 0.1% Ti tensile bar.

Authors theorizing that the titanium carbo-nitrides act as heterogeneous nuclei cite Bramfitt's original work on heterogeneous nucleation.[5] In Bramfitt's experiments, he immersed powders of materials in a steel melt under an argon atmosphere. The melt was then allowed to solidify around the powder. This is a very different situation than what happens in a steel casting. The only way for a particle to assist the nucleation of solid steel is if it is present before solid steel begins to form. For that to happen, there must be a thermodynamic driving force for the particle to form.

To determine if and when titanium carbo-nitrides are likely to form, the author conducted a Schiel solidification analysis using Thermo-Calc. Table 2 lists the steel chemistry used based on the actual steel chemistry of the castings and assuming a small amount of nitrogen is present in the steel. A fast diffusion assumption was employed with carbon and nitrogen to account for their high diffusivity. The calculation was done over the solidification range of the alloy. In addition to solid fraction, the phases present during freezing were calculated.

Table 3 Steel chemistry used for Schiel analysis.

C (wt. %)	Mn (wt. %)	Al (wt. %)	Ti (wt. %)	N (wt. %)
0.30	0.065	0.05	0.10	0.002

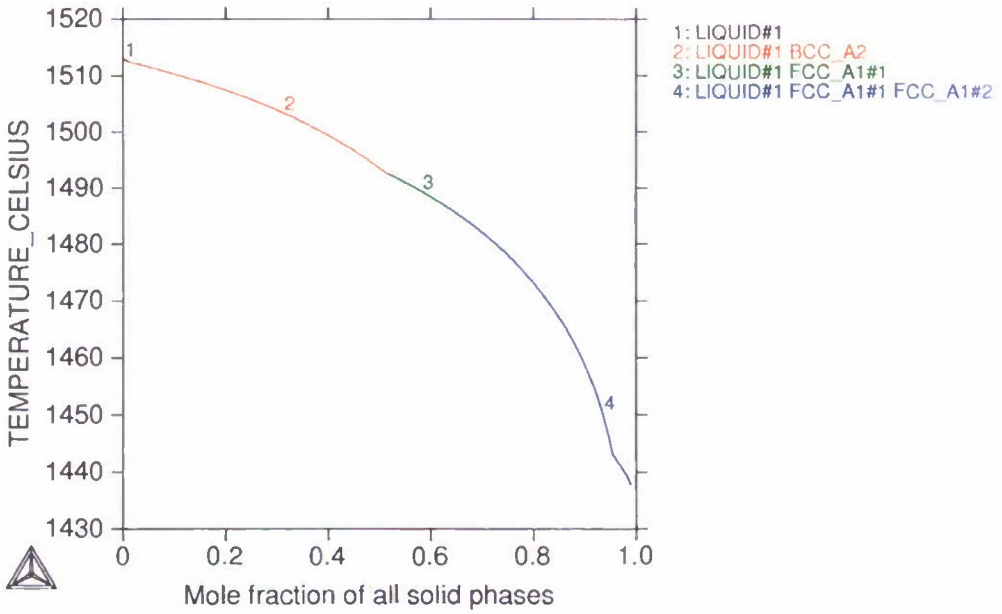

Figure 23 Schiel solidification analysis for 0.1% Ti containing 1030 steel.

Figure 25 depicts the results of the Schiel calculation. The BCC_A2 phase is δ-ferrite, FCC_A1#1 is austenite, and FCC_A1#2 is a titanium carbo-nitride. The Schiel analysis predicts the formation of δ-ferrite first. There is a small region where only austenite is present. No titanium carbo-nitrides are predicted to form until approximately 60% of the steel has solidified. This means that titanium carbo-nitrides are formed in the interdendritic liquid. At this point in the steel's solidification, the titanium carbo-nitrides would not act has heterogeneous nuclei for most of the solid formed. The carbo-nitrides could surround the already existing dendrites at the end of solidification. It is also possible that these titanium carbo-nitrides could restrict the grain growth of the austenite dendrites as they cool to room

temperature.[11,12] Titanium carbo-nitrides are known to restrict austenite grain growth in high strength low alloy (HSLA) steels.[12]

Austenite grain growth restriction as the casting cools would explain the observations in this work and Wallace's work. In both cases, the grain size decreased and strength increased with the addition of titanium. However, elongation decreased. The strength increase is likely due to the smaller grain size. The ductility loss could be caused by the carbo-nitrides formed. It is well known that large ceramic phases surrounding grains reduce the ductility of metals.

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Rare Earth Experiments

A set of rare earth addition experiments were also conducted. The concept behind these experiments was to form rare earth oxides in-situ in the ladle. Rare earth additions were conducted by adding 0.1% or 0.2% misch metal or rare earth silicide to the ladle during tapping. Melting and pouring were carried out as outlined in the titanium addition plate casting experiments. Experiments have been conducted in 1010 and 1030 during Fiscal Year 2010.

Table 4 presents the Rockwell B hardness measurements for these heats. Rare earth additions increased hardness in most cases. The 1010 with 0.2% rare earth silicide has a very high strength but this is

primarily due to a much higher carbon content than desired. One interesting problem is shown by the 1010 0.2% misch metal hardness data. The PI has had trouble repeatedly obtaining the strengthening with the rare earth additions. Several of the experiments had to be redone to obtain valid results. At this time, the PI does not understand the source of this variation.

Table 4 Rockwell B hardness measurements for rare earth addition heats.

Alloy	Hardness (HRB)
1010	42.58
1010 0.1% misch metal	51.46
1010 0.2% misch metal	40.2
1010 0.1 % RE silicide	52.26
1010 0.2% RE silicide	64.08
1030	74.08
1030 0.1% misch metal	79.16
1030 0.2% misch metal	81.38
1030 0.1% RE silicide	76.6
1030 0.2% RE silicide	83.42

Microstructural observations found a reduction in final grain size in both the 1010 and 1030 samples (See Figures 24-27). These grain size reductions do correspond to an increase in hardness. The PI is awaiting tensile testing results to understand how these structure changes affect the mechanical properties of these steels.

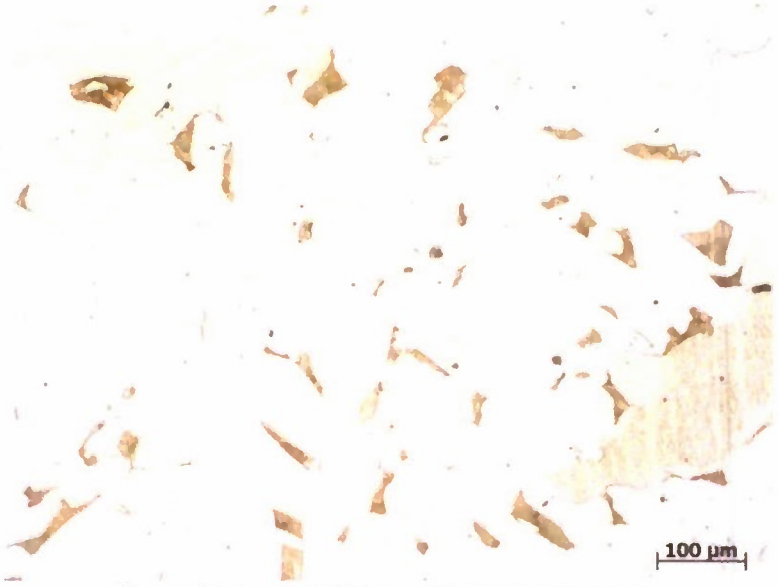

Figure 24 As-cast 1010 no addition micrograph.

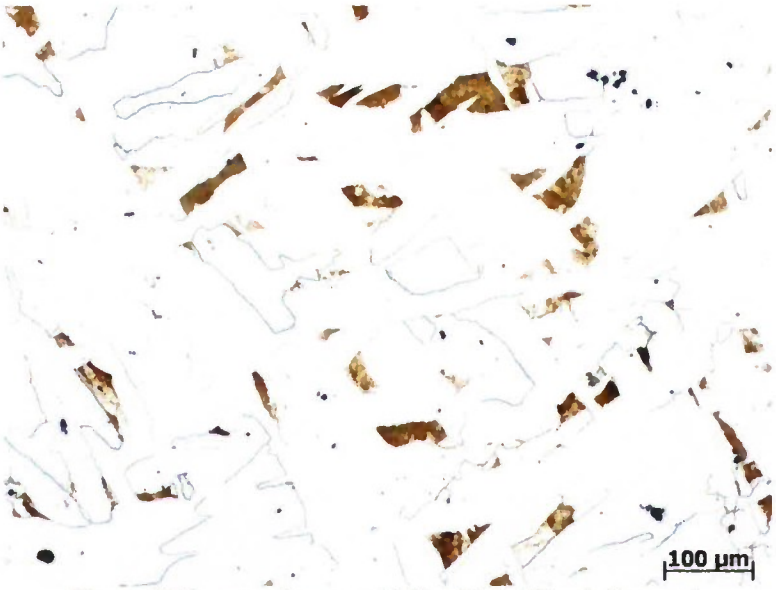

Figure 25 Image of as-cast 1010 with 0.1% misch metal.

Figure 26 As-cast 1030 no addition image.

Figure 27 As-cast 1030 with 0.1% misch metal addition micrograph.

REPORT DOCUMENTATION PAGE

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14. ABSTRACT
The overall research objective of this project is to determine suitable grain refiners for cast steels. Specific objectives are:
1) Identify possible phases to grow delta ferrite and austenite using current nucleation theory, crystallographic data, and thermodynamics.
2) Experimentally verify the effectiveness of possible nucleating compounds.
3) Extend grain refinement theory and solidification knowledge through experimental data.
4) Determine structure property relationships for the examined grain refiners.
5) Formulate processing techniques for using grain refiners in the steel casting industry.

15. SUBJECT TERMS
steel, casting, foundry, grain refinement, mechanical properties, solidification, and heterogeneous nucleation

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